Large Length Scale Structure in Laponite Gels and Block Polyelectrolyte Solutions

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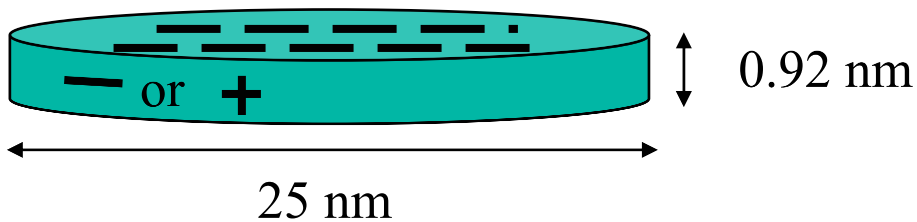
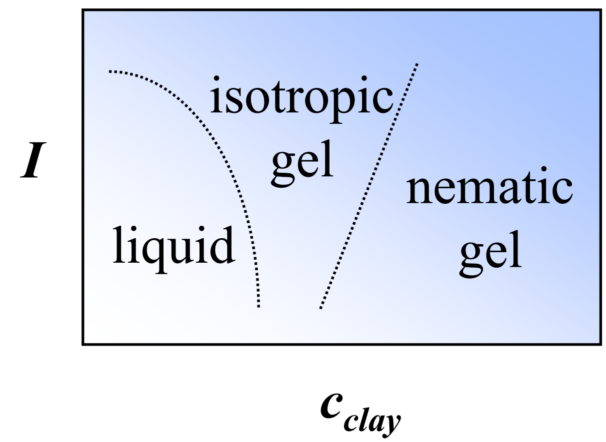
Clay Dispersions

Ahmed Mourchid (CNRS), John Barker (NIST)

- Applications of clay-based formulations
  - Paints, coatings, glazes,sunscreens, toothpaste, shampoos
  - Household and industrial cleaners
  - Polymer-clay nanocomposites
- Laponite: Synthetic hectorite clay



Phase diagram at pH = 10
Mourchid et al.,
Langmuir, (1998)



- Model anisotropic colloid and colloidal gel/glass
  - Faces carry net negative charge
  - Edges negative or positive, depending on pH (negative under basic conditions)
- Under basic conditions with no added salt, formation of isotropic elastic solid at $c_{clay} \sim 2$ wt%

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Mechanism of Gel Formation

- Structure of gel and nature of interparticle interactions debated
  - Attractive quadrupole or van der Waals forces lead to aggregate formation, or
  - Electrostatic repulsions generate a jammed, glass-like solid
- Conflicting results from scattering studies
  - Apparent fractal dimension of 1.8-2.8 via low *q* SAXS and static light scattering, with aggregates of ~ 1 μm (Pignon *et al*., 1997; Kroon *et al*., 1998)
  - Questioning of fractal dimensions from SAXS; SLS "nearly flat" indicating no large-scale structure (Bonn *et al*., 1999)
  - Aging and dynamics via diffusing wave spectroscopy consistent with repulsive interactions and formation of colloidal glass (Knaebel *et al*., 2000)
- No direct measurements of interparticle interactions
  - Osmotic pressure measurements consistent with repulsive interactions

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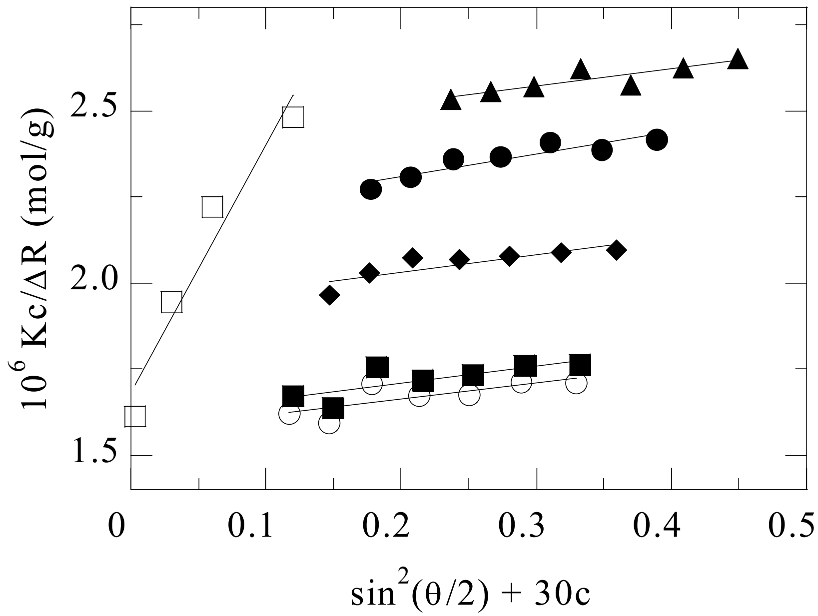
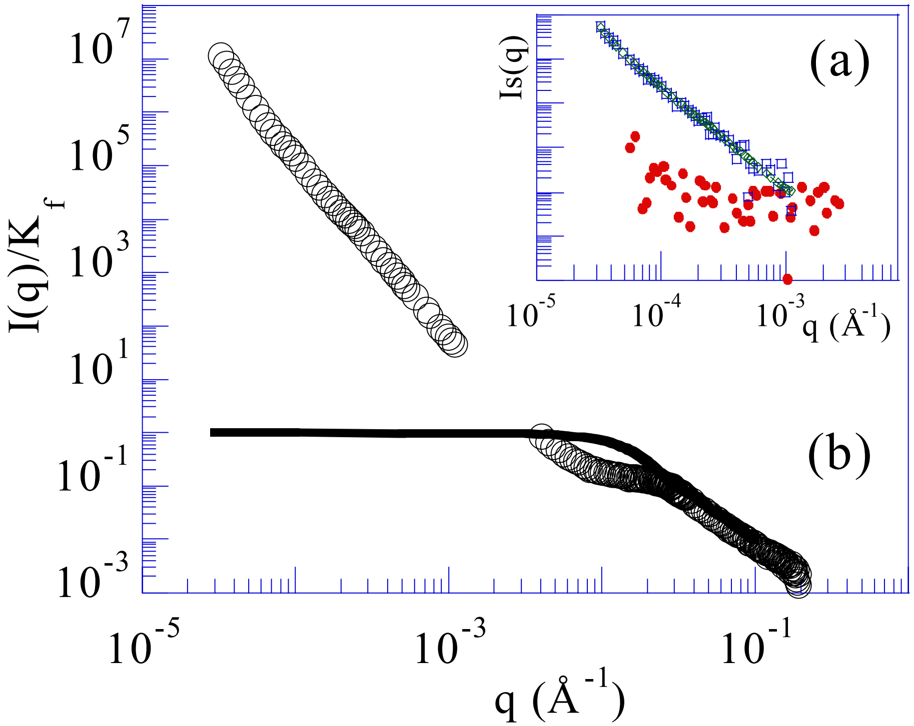
Interparticle Interactions

- Static light scattering using conventional Zimm plot for $c = 0.01 - 0.4$ wt%, pH = 10, no added salt



- Yields a second virial of 6×10^{-23} m^3, corresponding to repulsive interactions
- Good agreement with recent theories and computations for the thermodynamics of hard disks
- Consistent with osmotic pressure results

Can USANS Resolve the Debate?



pH = 10
No added salt
Filtered prior to gelation

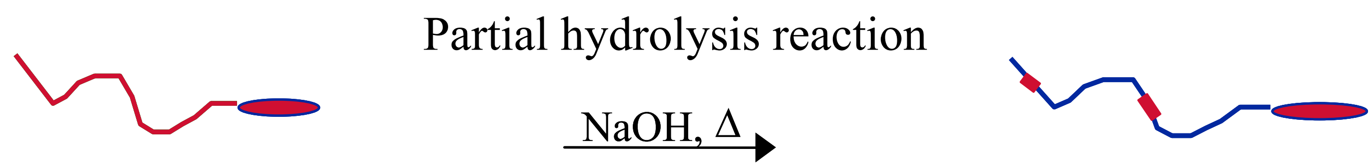
Bhatia, S.; Barker, J.; Mourchid, A. *Langmuir* **2003**, *19,*532.

- SANS and desmeared USANS on gels at 6 wt%, with form factor for disks with *d* = 28.0 nm and *l* = 1.0 nm
- Power law scaling observed at low *q* over two decades in *q* - large-scale structure **is** present in laponite gels, even without attractive interactions

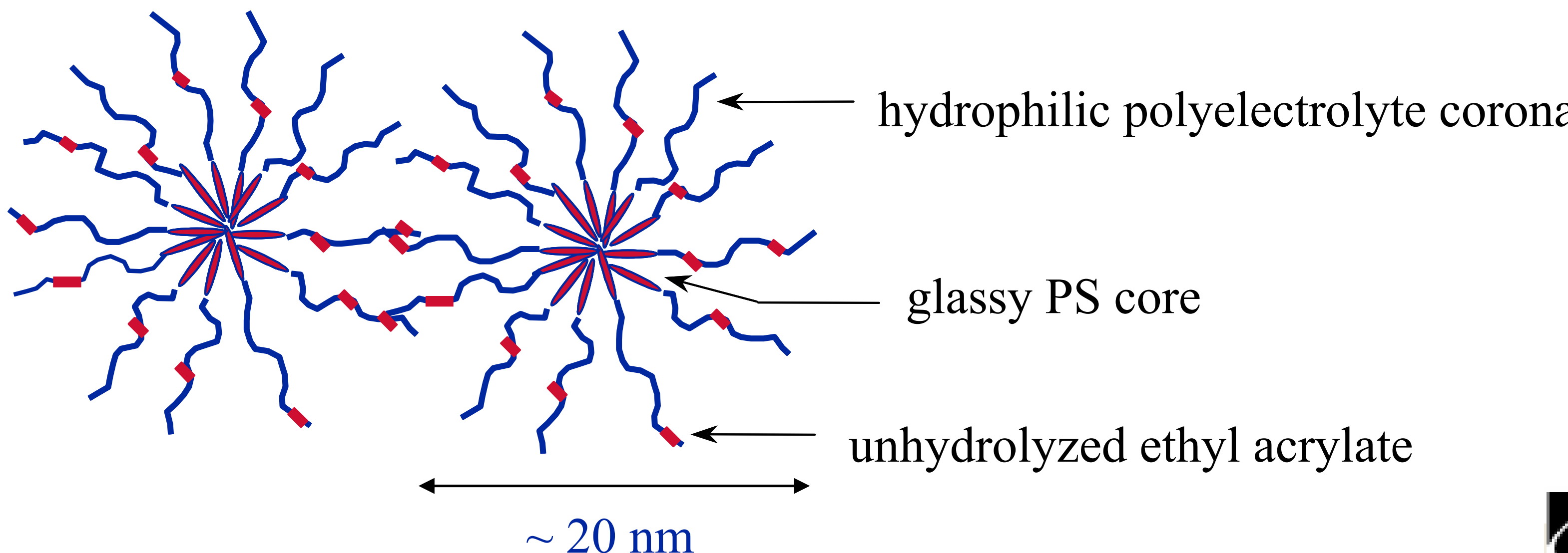
Block Polyelectrolyte Micelles

Mark Crichton (UMass), Rhodia Complex Fluids Lab

- Block polyelectrolytes in personal care products, biomaterials, etc.
- Poly(styrene)-poly(ethyl acrylate) (Rhodia Inc., Cranbury, NJ)



- Partial hydrolysis leads to PS-P(AA/EA) diblock
- Micellar structure in aqueous solution (pH = 9 - 10)



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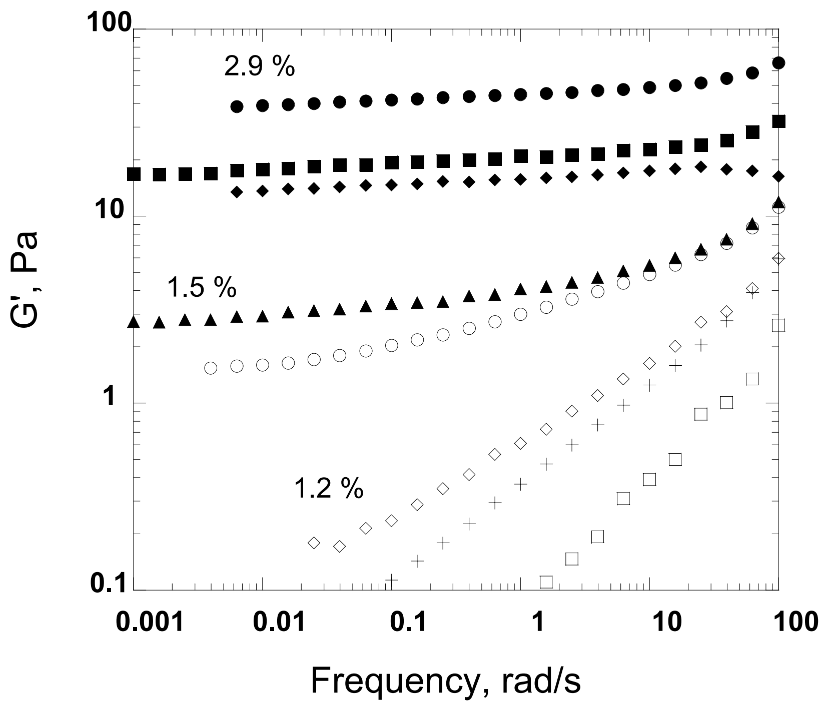
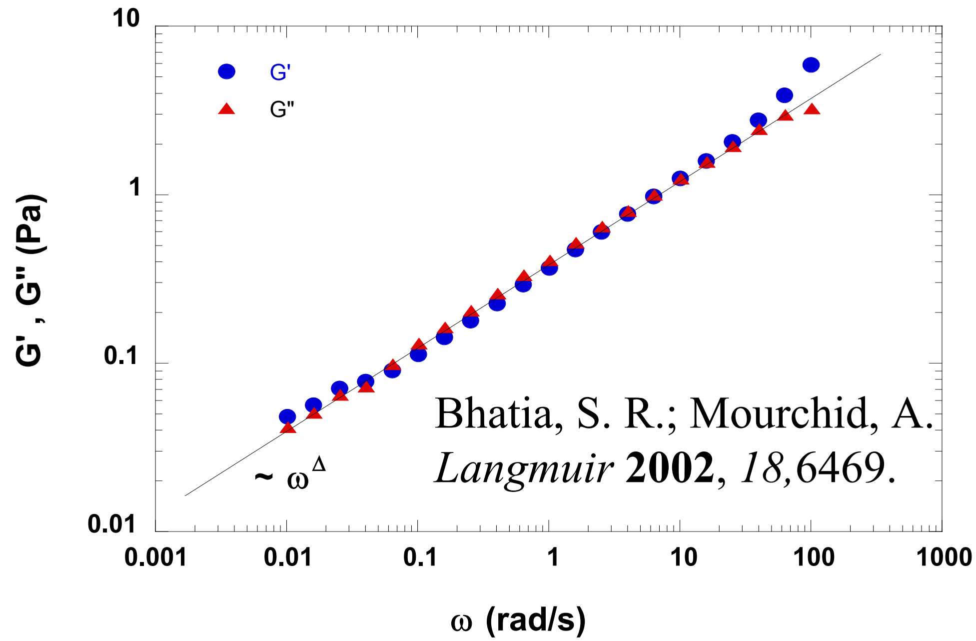
Rheology

- Transparent, elastic gels at low concentration (2 - 3 wt%)



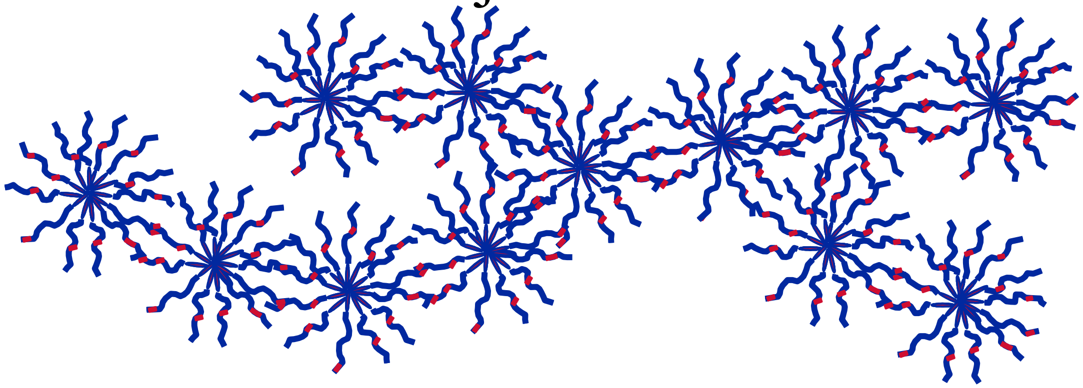


Bhatia, S. R.; Mourchid, A. *Langmuir* **2002**, *18*,6469.

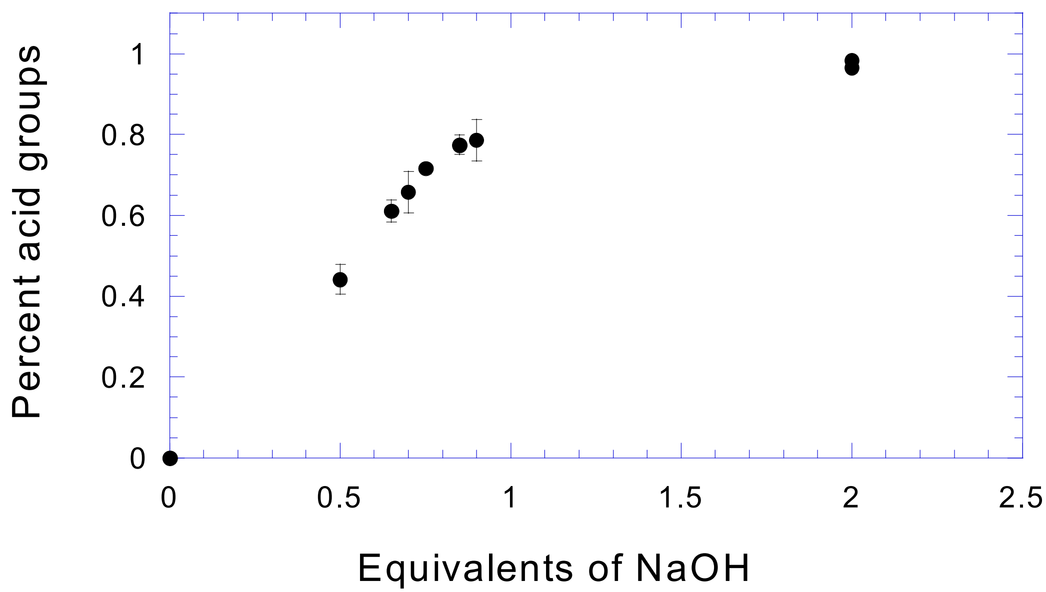
- Transition from viscoelastic liquid ($G' \sim \omega^2$) to a gel
- Power law scaling at gel point, similar to percolated network or colloidal glass ($G' \sim G'' \sim \omega^{0.51}$)
- How to control and tune rheological properties? Relation between intermicellar potential, microstructure, rheology

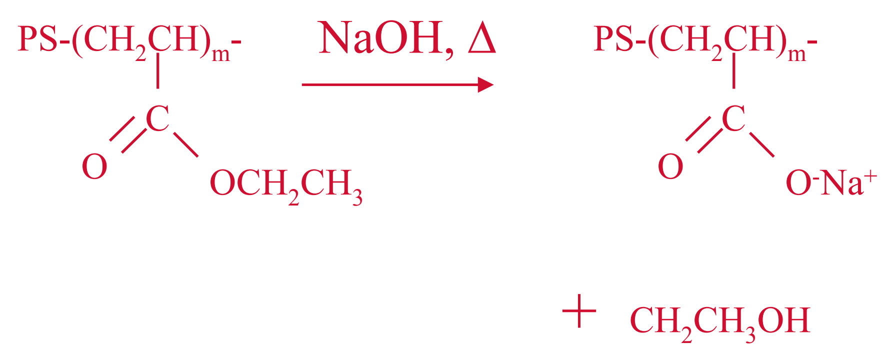
Controlling Attractive Interactions

- Associations between unhydrolyzed EA “stickers” form networked solution or jammed solid

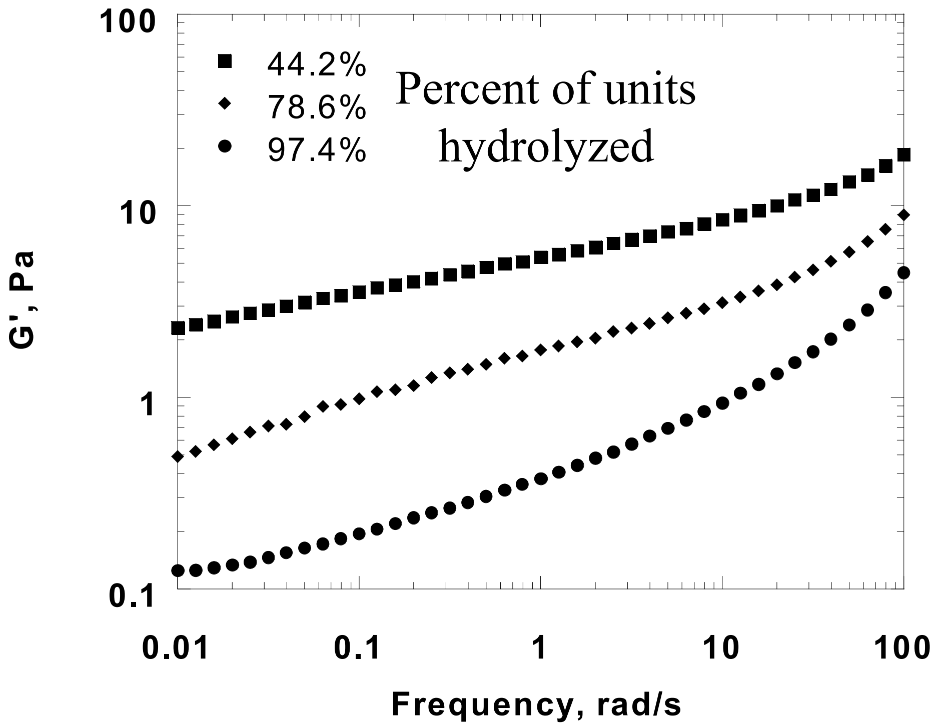


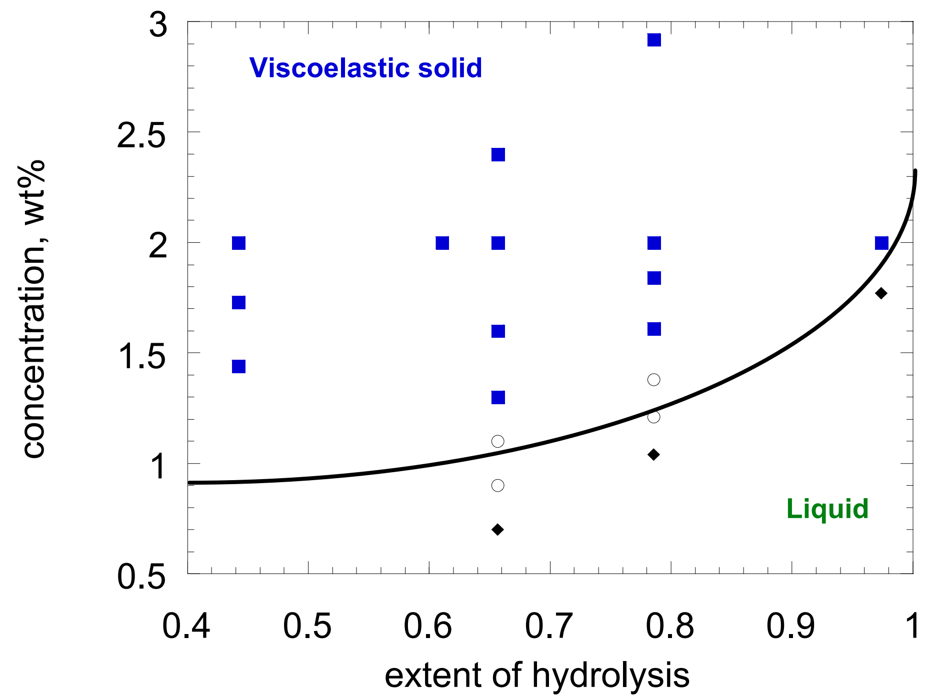
- Vary number of “stickers” via hydrolysis reaction: poly(ethyl acrylate) to poly(acrylic acid)





Impact on Rheology and Gel Boundary





Bhatia, S. R.; Mourchid, A.; Joanicot, M. *Current Opinion in Colloid and Interface Science* **2001**, *6*, 471-478.

- Elastic modulus increases as percent of “stickers” increases (percent hydrolysis decreases)
- Solid line indicates “critical gel” with power law scaling
- Transition between liquid and viscoelastic solid triggered by either concentration or extent of hydrolysis

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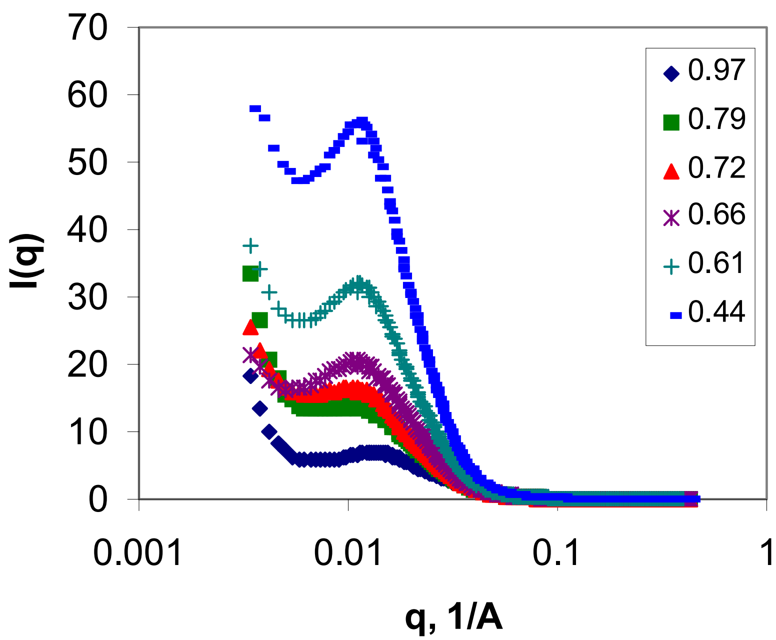
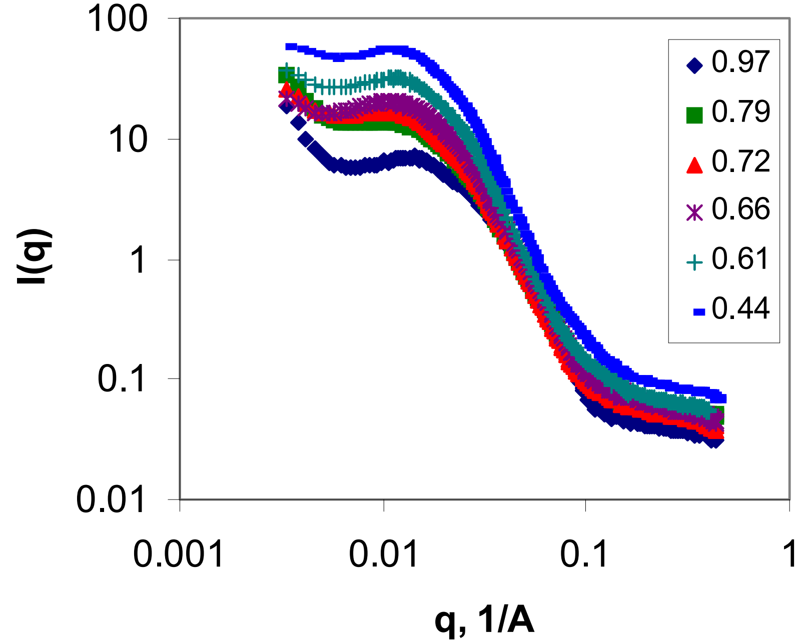
Micellar Structure: SANS Studies

- Gels at 4.0 wt% in D2O, NG3 instrument at NIST





- Relatively broad peaks with no long-range order
- Little change in peak position with extent of hydrolysis; increase in intensity and decrease in width
- Fit with spherical or core-corona form factor and adhesive hard sphere structure factor yields slight decrease in R_{mic} and N_{agg} with degree of hydrolysis

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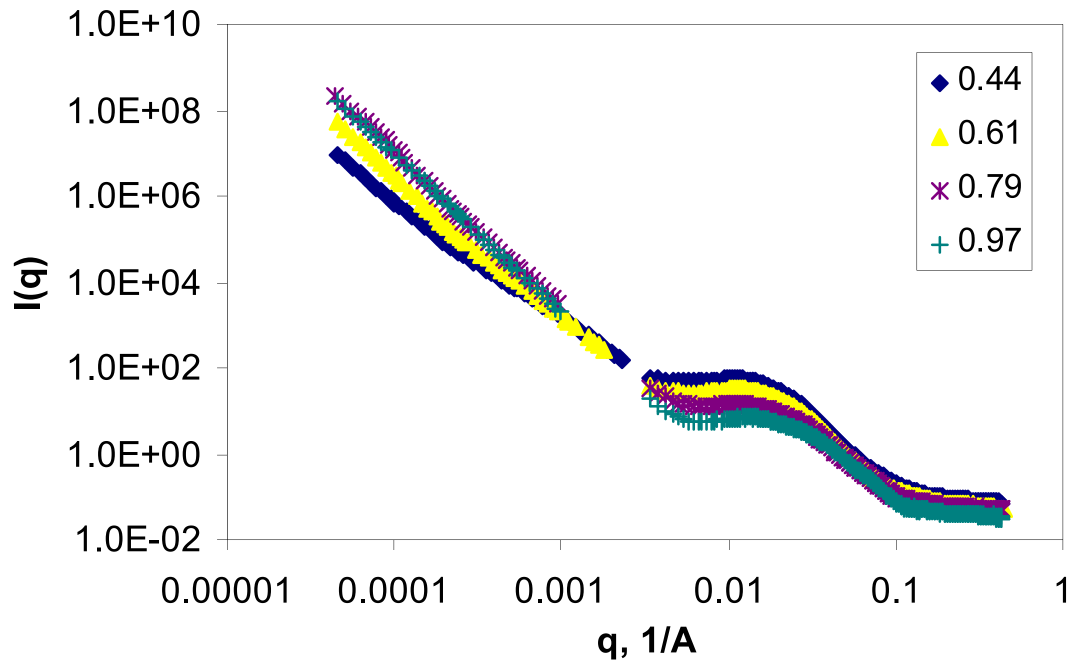
USANS Results (NIST)



Crichton, M.; Bhatia, S. R. *J. Appl. Cryst.* **2003**, *36*, 652-655.

- Power-law behavior at low *q*, with exponents increasing to ~ 3.7 for fully hydrolyzed system
- Large aggregates of micelle with fractally rough surfaces
- Similar to scaling seen in block polypeptide gels (D. Pochan and co-workers)

Conclusions and Future Directions

- USANS can contribute to the solution of into outstanding problems in soft matter
  - Gelation in colloidal systems
  - Jammed granular systems
  - Physical gels and networks of polyelectrolytes and biopolymers
- Complementary characterization yields new microstructure-property relationships
  - Connection to rheological properties
  - Solution/interparticle interactions
- Insight into data interpretation necessary to expand utility of USAS techniques

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